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## Diffusion in Crystalline Composition-Modulated Films

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### Abstract

The diffusivity in alloys at low temperatures is modeled for composition-modulated structures using Khachaturyan's microscopic theory of diffusion. The theory is now applied to assess a two-phase multilayer system.

### Introduction

A composition-modulated structure is composed of an artificial concentration wave as, e.g., formed by a repeating and alternate vapor deposition of the constituents.[1] The interdiffusivity coefficient ( $\check{D}_B$ ) is determined by analyzing the decay of the composition fluctuation (from thermal anneal treatments) using the microscopic theory of diffusion.[2-5] The bulk diffusivity ( $\check{D}$ ) represents the long wavelength approximation of  $\check{D}_B$ . That is, a multilayer with an infinite composition wavelength is equivalent to a macroscopic diffusion couple. A curvilinear fit to the variation of the  $\check{D}_B$  with the dispersion relationship ( $B^2$ ) yields  $\check{D}$  (at  $B^2$  equal to zero).[1,5] The dependency of  $\check{D}_B$  on structure is evident in the derivation for  $B^2$  that accounts for the specific growth orientation and composition wavelength of the multilayer accounting for the possible effects of crystalline anisotropy. Diffusion kinetics are quantified using x-ray scattering measurements. Satellites about Bragg reflection(s) are a consequence of the difference in scattering intensity that results from the short-range order, i.e. the composition modulation along the growth direction of the film. Also, grazing-angle satellites can be used for assessing the diffusion kinetics as, e.g., of amorphous layered structures.[6] For crystalline multilayer materials, the high angle Bragg reflection(s) ideally provide the crystallographic reference required to appropriately determine  $B^2$ . The advantage of the discrete theory in comparison to the continuous theory is its application to describe ordering, spinodal decomposition, and artificial composition modulations in disordered solutions where the behavior at short wavelengths is of interest. In addition to the treatment of fcc and bcc single-phase multilayers, as Cu/Ni [7] and Cr/Ti [8], the microscopic theory of diffusion is presented to assess the two-phase face-centered-cubic (fcc)/body-centered cubic (bcc) multilayer combination of Ni/(Cr,Mo) [9]. The low-temperature diffusion data from composition-modulated films provides a direct comparison with high-temperature tracer diffusion results [10].

### Theory

The integrated satellite intensity  $I^i(t)$ , each of reflection order (i), is normalized to the Bragg peak intensity  $I^B(t)$ . The decrease in  $I^i(t)$  for the annealed samples with time (t) indicates a progressive homogenization of the composition fluctuation. The satellite intensities are proportional to the square of the composition profile amplitude. The relative decay in satellite intensity determines the amplification factor  $R(k)$  according to the expression [1-5]

$$\ln\{I^i(t) \cdot [I^i(0)]^{-1}\} = 2R(k) \cdot t. \quad (1)$$

The  $R(k)$  is related to the generalized interdiffusivity  $\check{D}_B$  through the dispersion relationship  $B^2(k)$  as [4]

$$R(k) = -B^2(k) \cdot \check{D}_B. \quad (2)$$

The dispersion relationship  $B^2(h)$  for fcc growth along the [100] or [111] is given by [4]

$$B^2(h) = 2 \{1 - \cos(2\pi h)\} \cdot d_{(hkl)}^{-2} \quad (3)$$

where  $d_{(hkl)}$  is the Bragg-reflection interplanar spacing, h equals  $d_{(hkl)} \cdot (d_{A/B})^{-1}$ , and the composition wavelength for an A/B fluctuation ( $d_{A/B}$ ) equals  $2\pi \cdot k^{-1}$ . Again, the dispersion relationship  $B^2(h)$  for bcc growth along the [100] or [110] is represented by eqn. (3) whereas for [111] bcc growth the dispersion relationship is given by [4]

$$B^2(h) = 2 \{1 - \cos^3(2\pi h)\} \cdot \{3d_{(hkl)}^{-2}\}^{-1}. \quad (4)$$

The dependency of the  $\check{D}_B(s)$  on structure is found in the expressions for  $B^2$  which account for the multilayer periodicity and crystalline orientation. It may first appear at long wavelengths ( $d_{A/B}$ ) that  $\check{D}_B$  will decrease linearly with  $B^2(h)$  or perhaps inversely proportional to  $B^2(h)$ . [5-6] However, the use of a higher-order polynomial relationship is shown to universally fit the behavior of  $\check{D}_B$  with  $B^2(h)$ . Thus,  $\check{D}$  is related to  $\check{D}_B$  by the expression [5,9]

$$\check{D}_B = \check{D} \cdot \{1 + F_e(h) \cdot (f'')^{-1} + 2(f'')^{-1} \cdot \Sigma[K_\mu \cdot B^{2\mu}(h)]\} \quad (5)$$

where  $F_e(h)$  is the Fourier transform of the elastic strain energy of the distorted lattice,  $f''$  is the second derivative with respect to composition of the Helmholtz free energy per unit volume,  $\mu$  is the order of the polynomial, and  $K_\mu$  are the gradient-energy coefficients. In the long wavelength approximation,  $-B^2(h)$  equals  $k^2$ . Also,  $f''$  and  $K_\mu$  are identical with the expressions appearing in the continuous

theories [11] or the discrete theory [12]. An expansion of the series expression for eqn. (5), yields

$$\check{D}_B = \check{D} \cdot [1 + K_1 \cdot B^2(h) + K_2 \cdot B^4(h) + K_3 \cdot B^6(h) + \dots] \quad (6)$$

where  $K'_\mu$  equals  $2K_\mu \cdot [f'' + F_e(h)]^{-1}$ . A plot of  $\check{D}_B$  versus  $B^2(h)$  fitted with a polynomial curve using eqn. (6) determines the diffusion coefficient  $\check{D}$ .

## Results

Ni(111)<sub>24</sub>/(Cr<sub>2</sub>Mo)<sub>14</sub> multilayers are annealed to decay the composition modulation.[9] The Cu  $k\alpha$  x-ray diffraction scans (of Fig. 1) taken in the  $\Theta/2\Theta$  mode reveal the change of the satellite intensities with anneal time at 760 K. The two-phase (111)fcc/(110)bcc growth of the as-deposited 8.1nm composition-wavelength film is confirmed in the (Fig. 2) electron diffraction pattern as taken in plan view.

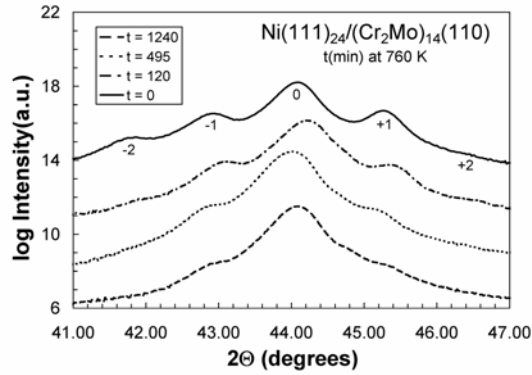


Figure 1. X-ray diffraction scans of the Ni/(Cr,Mo) film.

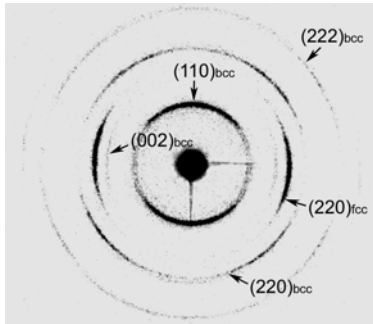


Figure 2. An electron diffraction pattern of the as-deposited 8.1nm Ni/(Cr,Mo) multilayer film.

The normalized intensity of the ( $i=-1$ ) satellite peaks for the Ni/(Cr,Mo) multilayers are plotted (in Fig. 3) as a function of the anneal time at 760 K for composition wavelengths of 8.1 nm (from Fig. 1) as well as 5.0 and 3.3 nm.[9] The  $R(k)$  value for each is determined from eqn. (1) using a linear regression procedure to fit the variation of  $\ln\{I^i(t)/[I^i(0)]^{-1}\}$  with time.[5,9] Also, results are presented for a 0.9nm Ti/Cr film annealed at 473 K and a 2.1nm Cu/Ni film annealed at 673 K.[7-8] Eqn. (3) is used to determine a single value of  $B^2$  for each fcc/bcc Ni/(Cr,Mo) multilayer. The  $\check{D}_B$  values are next computed using eqn (2). A fit of the  $\check{D}_B$  variation

with  $B^2$  is accomplished using eqn (6) to yield the  $\check{D}$  value of  $3.3 \times 10^{-19} \text{ cm}^2 \text{ sec}^{-1}$ . A classic Arrhenius variation of  $\check{D}$  with  $T^{-1}$  (plotted in Fig. 4) demonstrates the consistency of the low-temperature multilayer results obtained through the microscopic theory of diffusion with the high-temperature tracer diffusion data [10].

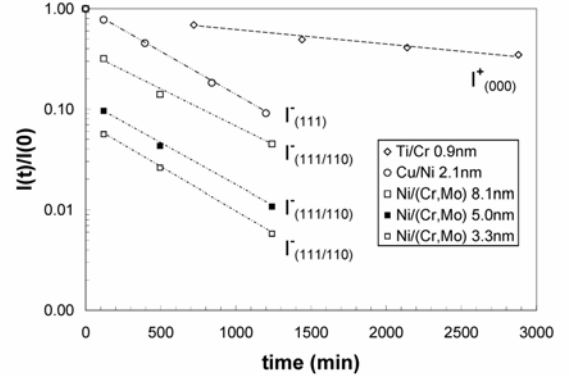


Figure 3. The satellites intensities decay with anneal time.

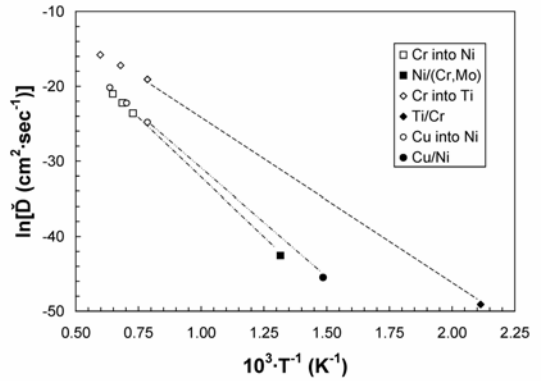


Figure 4. The variation of  $\ln[\check{D} (\text{cm}^2 \text{ s}^{-1})]$  with  $T^{-1} (\text{K}^{-1})$  is plotted for tracer- and multilayer-diffusion data.

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